

Integrity of Wellbore Cement in CO₂ Storage Wells

State of the Art Review

ANLEC Project 3-1110-0084

Luke Connell, Deasy Heryanto, Nicholas Lupton

28 May 2012

Report prepared for Australian National Low Emissions Coal Research & Development

Copyright and disclaimer

© 2012 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

Acknowledgments

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and The Australian Government through the Clean Energy Initiative.

Contents

Executive summary	iv
1 Introduction	6
2 Cement degradation mechanisms	8
3 Laboratory experimental studies	11
4 Conclusions	14
References	16

Executive summary

Wells are the key technology for both storing CO₂ and monitoring its reservoir migration. However new and existing wells could also represent a risk to storage assurance by potentially providing leakage pathways. Well construction involves the use of cement for two main functions; to cement well casing in place and to plug wells that are abandoned. CO₂ could leak from abandoned wells by flowing through a degraded, damaged or incomplete plug or outside the casing, between the casing and the formation. While one outcome is that CO₂ could migrate directly to surface via the well there is also the potential for CO₂ to migrate to other formations which may not have appropriate geology to prevent subsequent leakage or may contain other resources.

There are three main pathways for CO₂ leakage between the casing and the formation; the interface between the cement and the formation, within the cement itself or the interface between the cement and well casing. While poor cementing practices during well completion may represent an important opportunity for the creation of migration pathways, there is also potential that cement degradation over long time periods could create pathways in otherwise soundly cemented wells. The focus of the current report is on the previous work related to the potential for cement to degrade to the extent that storage assurance is compromised rather than on completion practices.

CO₂ injected into a saline aquifer will displace formation water and over time regions will develop of essentially pure CO₂ and also formation water with dissolved CO₂. The potential exists for both these fluids to come into contact with wells. The process of interest in cement degradation is carbonation which involves a series of chemical reactions. Previous work by Kutcho et al. (2008) found that the reaction potential of CO₂ saturated water is much more significant than pure phase CO₂. This is a result of the dissolution of CO₂ into formation water leading to carbonic acid. The resultant formation water can have a pH of between 3 and 4, depending on the water chemistry and the reservoir pressure and temperature, with an acidity comparable to orange juice. The solubility of CO₂ in water is a strong function of pressure and temperature; for seawater increasing from 0.03 mol/kg @ 20° Celsius and atmospheric pressure to 1.08 mol/kg @ 40° Celsius and 10 MPa (Duan et al., 2006). It is therefore important that experiments investigating cement carbonation properly represent the likely conditions within the reservoir.

Adequately cured cement has a very low permeability meaning that bulk flow of water through the intact cement matrix is extremely limited. Additionally one of the reaction products is a solid, calcium carbonate, which can precipitate and act to lower permeability. Thus under certain circumstances cement carbonation will be self sealing and act to prevent further cement degradation (Kutcho et al., 2008; Carey et al., 2010). However, this calcium carbonate can solubilise in the presence of dissolved CO₂ and thus could be removed if the pore fluids are flowing at a sufficient rate. The evidence from wells exposed to CO₂ over long periods is that CO₂ can migrate along the casing-cement or formation-cement interfaces and cause cement carbonation along these, however the initial permeability along these

interfaces could be a result of other mechanisms rather than CO₂ induced degradation (Carey et al., 2007; Crow et al., 2009).

Previous laboratory experimental work can be divided into static experiments where cement is exposed to acidic waters in a batch reactor or dynamic experiments where water flows through a sample. An important difference between these experiments is that in the static experiments the migration of acidic pore waters and reaction products is limited by diffusion in the cement matrix. In contrast the dynamic experiments involve flow of pore fluids however this may also be limited in the case of intact cement matrix due to its low permeability. An important question is what is most representative of reservoir conditions and it is possible that both static and dynamic conditions could occur during CO₂ storage. The dynamic conditions will be most conducive to cement degradation since there is the potential for fresh unreacted formation fluid to be brought into contact with the cement and for reaction products to be removed.

While there have been a number of static experiments, dynamic experiments at pressures, temperatures and water chemistries representative of reservoir conditions are much more limited. Previous dynamic work has considered the cement-casing interface (Carey et al., 2010) and migration through cement (Bachu and Bennion, 2009). For both cases precipitates formed during the reaction have acted to clog the migration pathways. A missing aspect to this previous work is the cement-formation interface where there is potential for flowing pore waters rich in CO₂ to come into contact with the cement. At this interface, for a permeable formation, degradation products could be dissolved and removed potentially leading to an erosion of the cement over time. However, for where wells are within the seal to the storage formation flow rates will be low. While experiments conducted by Duguid et al. (2011) considered the cement-formation interface these were essentially of a static nature in a batch reactor at atmospheric pressure and ambient temperature. In order to replicate the acidity of pore waters at reservoir pressures and temperatures Duguid added HCl to the water in the experiments to lower its pH.

The review has identified that dynamic experiments, involving fluid flow, at reservoir pressures and temperatures and with representative formation water chemistry are important to ensuring that the work is representative of the National Storage Flagship sites. The number of dynamic studies at reservoir pressures and temperatures has been limited with more work presented from static experiments. An important aspect for the experimental work will be the cement-formation interface as this has not been considered using dynamic experiments. Since water flow rates and CO₂ concentrations will play important roles in the cement carbonation process, a key gap with existing experimental work is integrating the largely reservoir nature of these processes with the information from experimental studies. For example, it is CO₂ rich formation water that has the greatest potential to degrade wellbore cement, however this has a greater density than the virgin formation water and also the single phase CO₂, meaning that it will sink in the reservoir.

1 Introduction

Wells are the key technology for both storing CO₂ and monitoring its reservoir migration. However new and existing wells could also represent a risk to storage assurance by potentially providing leakage pathways (see Figure 1). The construction of wells involves the use of cement for two main functions; to cement well casing in place and to plug wells that are abandoned. CO₂ could leak from abandoned wells by flowing through a degraded, damaged or incomplete plug or outside the casing, between the casing and the formation (see Figure 2). While one outcome is that CO₂ could migrate directly to surface via the well there is also the potential for CO₂ to migrate to other formations which may not have appropriate geology to prevent subsequent leakage. It is difficult to estimate possible rates of leakage as this is determined by a broad range of factors but could be over a broad range, although large leaks could be expected to prompt corrective action. Given the long time frames involved with CO₂ storage even small leakage rates could lead to significant cumulative loss.

Cement degradation is the result of a series of reactions that take place when acidic formation water, resulting from CO₂ dissolution, comes into contact with the well. Depending on the solution chemistry this could lead to an increase in the porosity and permeability of the cement. There is also the potential for degradation to lead to a decrease in permeability as precipitates form in the cement porosity (Duguid, 2009). This process is complicated by the nature of CO₂ migration behaviour (and thus the exposure of cement to acidic formation waters), the formation geochemistry and temperature, and the actual cementing practices. While there is considerable evidence of cement degradation from laboratory experiments (i.e. Duguid, 2009; Kutchko et al 2008; Scherer et al., 2005; Bachu and Bennion, 2009), field studies have been more limited. In one study evidence was found of CO₂ migration and cement reactions in a well cement sample recovered from a 30 year old CO₂ Enhanced Oil Recovery well in Texas at the SACROC Unit (Carey et al., 2007). In another study, cement alteration due to CO₂ exposure was observed in samples from a well in a natural CO₂-rich gas field (Crow et al, 2009). In both cases, although there was an increase in permeability, the cement was still able to prevent significant vertical migration of CO₂. Carey et al. (2007) hypothesised that the CO₂ migration along the cement-formation interface could be the result of a poor bond due to the presence of filter cake rather than a flow pathway created by cement degradation. Cement composition plays a role in this process, with cement containing pozzolans (fly-ash) leading to a more rapid and uniform reaction with CO₂, while cement without pozzolans showed distinct reaction fronts and some self-limiting behaviour (Strazisar et al., 2009; Kutchko et al 2008).

If CO₂ migrates along existing interfaces (e.g. casing-cement or cement-formation) or fractures within the cement (Wigand et al, 2009; Carey et al, 2010) geochemical alteration of the cement and corrosion of the casing will then be coupled with migration along these pathways. The open question is could these lead to an increase in the permeability of the pathway or could these be self-limiting due to precipitation and permeability reduction.

As discussed above it is CO₂ rich formation water that has the greatest potential to degrade wellbore cement. However this has a greater density than the virgin formation water and also the single phase CO₂, meaning that it will sink in the reservoir. This would mean that the acidic formation fluids would move away from critical areas such as the storage formation seal. Laboratory experiments to date have examined idealised situations in relation to the degradation process, what is required is to integrate these with the reservoir migration behaviour of CO₂ to assess where degradation could occur and the potential for this to lead to CO₂ leakage.

This document presents a review of the previous experimental studies on cement degradation as part of a research project funded under the ANLEC research program.

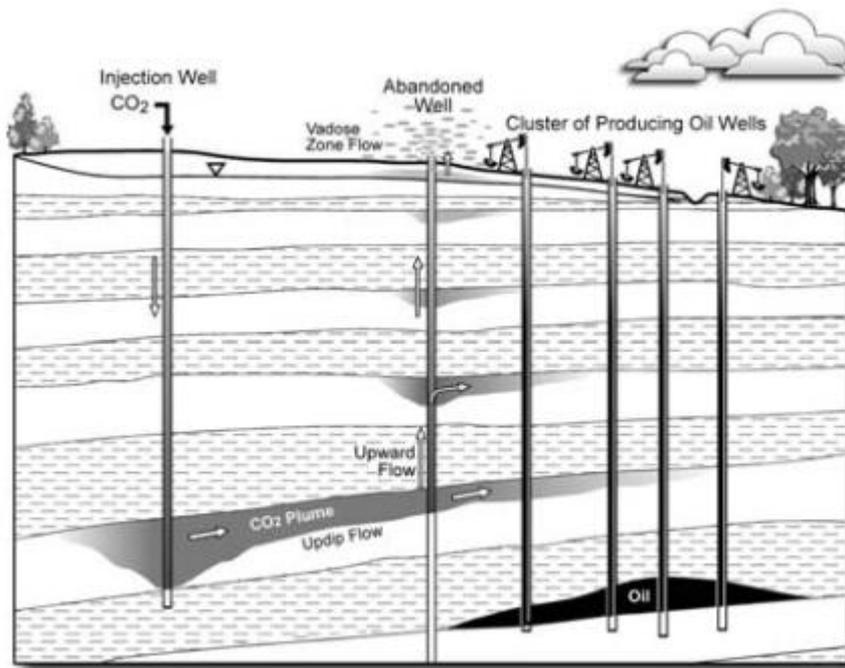


Figure 1. Schematic illustration of the CO₂ injection, migration and leakage (from Celia et al., 2004).

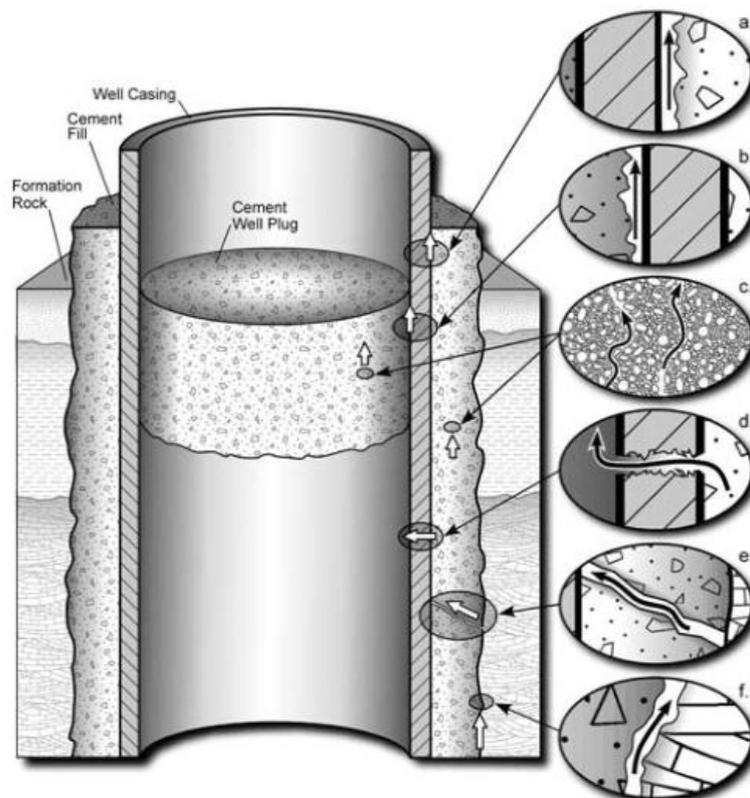


Figure 2. Conceptual illustration of the potential leakage pathways for CO₂ in a well; the casing-cement interface (paths a and b), within the cement (c), through the casing (d), through fractures (e), cement-formation interface (f) (from Celia et al., 2004).

2 Cement degradation mechanisms

Well cement chemistry

Cement is used to seal the annulus between the well casing and the formation rock. In this section, the following shorthand notation will be used in the description of the cement chemistry:

- C = CaO (calcium oxide)
- S = SiO (silicon oxide)
- A = Al₂O₃ (aluminium oxide)
- F = Fe₂O₃ (iron (III) oxide)

According to the API Specification for Cements and Materials for Well Cementing 10A, typical wellbore cements are generally made with Ordinary Portland Cement class G or class H. There are other cements available for wells, including products which may offer some resistance to aspects of the degradation process. However the discussion here is limited to the above for conciseness. OPC is composed primarily of four compounds: C₃S, C₂S, C₃A and C₄AF as defined in Table 1. Minor components include free lime (CaO), magnesia (MgO), sulphur trioxide (SO₃). The chemical composition of the Class G and H cement is set out in Table 1 and Table 2.

Table 1 Main Composition of Portland Cement

Compound Name	Composition	Abbreviation
tricalcium silicate	3CaO.SiO ₂	C ₃ S
dicalcium silicate	2CaO.SiO ₂	C ₂ S
tricalcium aluminate	3CaO.Al ₂ O ₃	C ₃ A
tetracalcium aluminoferrite	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	C ₄ AF

Table 2 Composition of Class G and H Cement

Chemical Composition		
	API 10A (%)	Typical Values* (%)
Insoluble residues	0.75 max	0.4
Sulphur trioxide (SO ₃)	3.0 max	1.9
Magnesia (MgO)	6.0 max	0.69
Alkali (Na ₂ O equivalent)	0.75 max	0.30
Tricalcium aluminate (C ₃ A) + Tetracalcium aluminoferrite (C ₄ AF)	24.0 max	20
Tricalcium aluminate (C ₃ A)	3.0 max	2.0
Tricalcium silicate (C ₃ S)	48.0 - 65.0 max	58

*Value are taken from Adelaide Brigton Cement, Class G cement.

Cement hydration processes

The hydration of wellbore cement to create a cement slurry should follow the API Recommended Practice 10B. For class G, a water to cement ratio of 0.44 should be used; and for class H, it should be 0.38.

The addition of water to well cement yields a range of products but the main products formed are calcium-silicate-hydrate (C-S-H) and calcium hydroxide (Ca(OH)₂ or abbreviated CH). C-S-H, often called the “gel phase” comprises approximately 70 wt% of the hydrated cement and has no fixed composition, but the average ratio of calcium to silicon is about 1.70 (Taylor, 1997). C-S-H is responsible for the strength of the hardened paste due to large covalent/ionic bonding (approximately 65%) and Van der Waals bonding (approximately 35%) within the complex structure .

Calcium hydroxide (CH) is crystalline with variable morphology from large, hexagonal prisms to thin, elongated crystals. CH comprises about 15-20% of hydrated cement and does not contribute much to strength. It is the CH that plays a significant role in the carbonation process as it can react with CO₂. CH keeps the pore solution alkaline at pH 12.4 – 13.5 (Scherer et al, 2005)

Both C₃S and C₂S hydrates into C-S-H, but C₃S hydration is more rapid and contributes to early age strength of the cement paste (2 hours to 7 days). C₂S hydration occurs more slowly and contributes strength after 7 to 14 days (Taylor, 1997). C₃S produces three times as much CH as C₂S in the following reactions:



C₃A and C₄AF react violently with water and can create a “flash set” which is a sudden hardening of the cement paste that can be avoided by adding gypsum to the cement mixture.

As the hydrated cement paste begins to set, the cement slurry is transformed to an elastic solid. As setting continues, the water is all consumed and the pores spaces are eventually filled with gel phases. At the setting point, the cement has approximately 28% porosity and pores ranging 2 to 10 nm in diameter. These capillary pores control the permeability of the paste. When the permeability is high, chemical attack of the hydrated paste can be very fast. A well-formed cement has a very low intrinsic permeability of the order of 10⁻²⁰ m² (approximately 10⁻⁵ mD) (Scherer et al, 2005)

Reaction with CO₂

In brief, reaction of hydrated Portland cement with CO₂ can be summarised as reaction of calcium hydroxide to give calcium carbonate, and the decalcification of the C-S-H to form calcium carbonate and an amorphous silica gel.

The first step is the dissolution of CO₂ forming carbonic acid, H₂CO₃, in the presence of water. If the CO₂ is in gaseous or supercritical state then salivation occurs within the cement, which is followed by a hydration step. Only a small proportion of the dissolved CO₂ will form carbonic acid and the capacity of water to dissolve CO₂ increases with pressure and decreases with temperature. The formation of carbonic acid changes the chemistry of the solution, decreasing the pH. Schaef and McGrail (2004) present measurements of the pH of CO₂-water with respect to pressure, temperature and salinity and found that

the pH ranged from 3.1 to 3.3 for pressures above 5.5 MPa and temperatures from 25° to 70°C. This pH is moderately acidic, similar to what you would find with orange juice or soda water. The following describes the dissolution of CO₂ and the formation of carbonic acid;



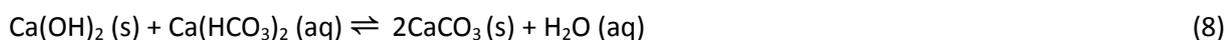
The crystalline form of calcium hydroxide (Ca(OH)₂) reacts with carbonic acid to form calcium carbonate, CaCO₃. The C-S-H gel also reacts to produce amorphous silica gel;



Of the polyform of calcium carbonate, vaterite and aragonite be formed, but these should ultimately revert to calcite (Bertos et al, 2004). The increase in molar volume from 26.2 cm³/mole for CH to 33.2 cm³/mole for CaCO₃ actually makes the cement stronger and less permeable. Precipitated calcium carbonate fills the available pore space resulting in a denser material.

However, degradation of cement with increased permeability and loss of strength is commonly observed in subsurface environments (Carey et al, 2007). If the exposure to carbonic acid is long enough or the carbonic acid is refreshed often or the leaching of CaCO₃ to flowing ground water is high, accelerated reaction of CH is expected. Since CH constitutes the alkaline reserve to acidic attack, removal of CH results in lower pH. The stability of the C-S-H gel is compromised when the pH drops below 10, and once the C-S-H is degraded, the result is a highly porous amorphous silica gel. As a consequence is a higher porosity and higher permeable cement. Increased porosity and permeability allow greater influx of aggressive agents, so the corrosion process accelerates.

Far more serious is the reaction of calcium carbonate to produce calcium bicarbonate as equation (7). Calcium bicarbonate is more soluble in water and can thus migrate out of the cement matrix through diffusion or the bulk flow of pore fluids. In addition calcium bicarbonate can react with CH as in equation (8);



3 Laboratory experimental studies

Batch vs flowing experiments

Laboratory experimental studies have focused on characterisation of well cement behaviour when exposed to CO₂. The types of laboratory experiments undertaken can be divided into two broad categories: batch type and flowing type experiments. Batch type experiments are designed to assess cement behaviour as a result of exposure to a stationary liquid (a CO₂ rich water or brine, or supercritical CO₂), representing static reservoir conditions in an abandoned well. Flowing type experiments are designed to assess cement behaviour during exposure to a CO₂ rich fluid under dynamic reservoir conditions. For example, flow through the cement, or along the cement-caprock interface or cement-casing microannulus.

Under static reservoir conditions, as represented by batch type experiments, several characteristics of cement behaviour have been examined. Studies by Onan (1984), Kutchko et al. (2007, 2008), Rimmele et al. (2008), Short et al. (2001) and Barlet-Gouedard et al. (2009) have examined the effect of exposure to CO₂ saturated water and supercritical CO₂ on pre-cured cement samples. Under these conditions cement alteration occurs. This alteration is characterised by a series of concentric fronts of carbonation and dissolution (Rimmele et al., 2008) penetrating from the fluid interface into the unaltered cement. During this penetration, initial precipitation of carbonates may plug the porosity and initially seal the cement. This stage will be followed by dissolution of carbonates which increases the porosity (Rimmele et al., 2008; Barlet-Gouedard et al., 2009). The rate and extent of penetration into the cement is dependent upon both the cement properties and the environment that it is exposed to.

The focus of this review will be on dynamic experiments where flowing pore fluids come into contact with the cement since these experimental conditions come closer to replicating the in-situ conditions which could maximise cement degradation processes and will be the focus of the experiments under this project.

Experimental conditions: pressure, temperature and water chemistry

As discussed above cement degradation or carbonation occurs as a result of coming into contact with carbonic acid formed from the dissolution of CO₂ into pore water. Thus the acidity of the pore water is an important attribute of the carbonation process and is directly related to the quantity of dissolved CO₂, which is in turn a function of pressure, temperature and the concentration of other dissolved compounds. Rochelle and Moore (2002) present measurements of CO₂ solubility with respect to pressure and temperature for distilled water and brines and found that these factors play a significant role in the solubility. Therefore, for cement carbonation experiments to be representative, they need to be conducted at representative pressures and temperatures and groundwater solution chemistry.

Choi and Netic (2009) found that CO₂ solubility in water was much higher than the solubility of water dissolved in CO₂ and as a result CO₂ dissolved in water had significantly higher rates of metal corrosion with little corrosion measured for the CO₂ rich experiments. While both states can occur within the reservoir, i.e. water as the dominant material with dissolved CO₂ or CO₂ as the solvent and water the solute, the mixture of interest is CO₂ dissolved in water since this can form the highest concentration of carbonic acid.

Environmental factors have a significant effect on cement degradation. Differences in the type of degradation have been observed between exposure to CO₂ saturated water/brine, or wet supercritical CO₂. With degradation as a result of exposure to supercritical CO₂ similar to contact with atmospheric CO₂, while exposure to CO₂ saturated brine was more typical of carbonic acid attack (Kutchko et al., 2008). In the same study, extrapolated penetration rates over 30 years of 1.00±0.07mm for CO₂ saturated brine and 1.68±0.24mm for wet supercritical CO₂ were observed. In addition, dissolution of the carbonated phases within the cement occurs earlier in CO₂ saturated water than in wet supercritical CO₂, and high salinity

brine was observed to slow the rate of alteration of exposed cement by a factor of 10 (Barlet-Gouedard et al., 2009).

Cement curing conditions

Cement properties such as the initial curing conditions (pressure and temperature), permeability and initial water content affect the extent of degradation that results from exposure to CO₂ saturated waters/brines. Kutchko et al. (2007) observed that cements cured at elevated temperature and pressure exhibited changes in the microstructure of the Ca(OH)_{2(s)} phase within the cement, making it more resistant to carbonic acid attack than cement cured at atmospheric pressure and temperature. This was attributed to the presence of smaller, more evenly distributed Ca(OH)_{2(s)} crystals providing a uniform and effective barrier to CO₂ attack. In addition, it was observed that cements cured with a lower initial water content displayed reduced amounts of carbonation, having been moisture equilibrated at 95% relative humidity and exposed to wet supercritical CO₂ (Short et al., 2001).

Cement carbonation experiments

Overview

There are several pathways that could potentially lead to CO₂ migration from a storage formation via wells, these include; leakage through the cement, or via the cement-casing interface, or along the cement-formation interface. While cementing practices during well completion would play a key role in the potential for these pathways, in this review we are interested in the cement degradation process itself as a primary focus for characterisation.

Cement-formation interface

While this is probably the main point of contact for stored CO₂ and wellbore cement, it has not received a great deal of attention in terms of laboratory studies to date. A study by Duguid et al. (2011) exposed cement samples embedded in sandstone and limestone to CO₂ saturated brine. Since these experiments were conducted at atmospheric pressure and 20° Celsius, the pH was adjusted further to that expected at reservoir pressures and temperatures by adding HCl. A flushed reactor vessel approach was used for this work where the brine was continuously replaced, and thus the reactant and reaction products diffused from the surrounding fluid into the cement-formation plug. This differs considerably from the likely arrangements in the reservoir where the brine would flow through the formation and come into contact with the cement at the cement-formation interface. Even for these artificial circumstances (atmospheric pressure and ambient temperature, flushed reactor style, artificial pore water chemistry) of these experiments it was found that the cement-formation interface may be subject to attack depending upon the mineralogy of the rock that makes up the host formation. Indeed, cement embedded in sandstone was shown to exhibit more damage than cement embedded in limestone, which showed no visible signs of attack and no increase in permeability after one year of exposure. In the limestone-cement experiments the water had been saturated with dissolved CaCO₃ prior to exposure to the cement to replicate the likely pore water chemistry within a limestone reservoir ; this meant that some of the carbonation reactions would be constrained. The same study also observed that samples exposed to lower pH brine showed the most and fastest damage compared to those exposed to the highest pH which is a logical relationship with the understood role of acids in cement carbonation.

Studies of cement behaviour under dynamic well conditions have considered the effect on cement only, and also the effect on cement-formation and cement-casing interfaces. Indeed, under dynamic conditions the reaction kinetics and dissolution of carbonates occur faster, as a new supply of low pH fluid reaches the carbonate layer (Yalcinkaya et al., 2011). Duguid & Scherer (2010) found that, similar to static conditions, cements exposed to flowing solutions representative of those found in either sandstone or limestone formations degraded differently. Again, cement is subject to rapid degradation under formation water equilibrated under sandstone-like conditions, while cement exposed to formation water equilibrated with limestone (calcium saturated fluids) showed no degradation. However it is likely that the formations within

the seal lithology could play the key role in formation-cement interactions since the well integrity would need to be compromised over the seal in order for leakage to occur via this route.

Migration within the cement

As noted in Chapter 2, cement, properly cured and un-degraded, has very low permeability, of the order of 10^{-5} millidarcy and thus bulk flow is negligible and migration diffusion limited. However, a fractured/degraded cement could have pathways, in the fractures, for the migration of CO_2 . Huerta et al. (2009) investigated the potential pathways within cement and observed that coupling between the reaction of cement to a CO_2 rich environment, and the cement's geomechanical properties strongly affects leakage rates through these pathways. Fractures measured for their conductivity at different confining stresses, were degraded with hydrochloric acid to simulate exposure to CO_2 saturated brine. Tests indicated that a fracture that is heavily reacted closes much faster as confining pressure increases with the permeability thus decreasing significantly. This in turn raises the possibility that leaks could be self sealing. Conversely, it has been observed that calcite precipitation in fractures may lead to a partial opening of the fracture, and a related increase in permeability (Wigand et al., 2009).

When flowing CO_2 saturated brine through cement, permeability changes were observed by Bachu and Bennion (2008). During core flooding experiments on cement plugs, the permeability dropped rapidly and remained constant thereafter. This reduction was attributed to the fact that low flow rates through the cement could not remove the products of carbonation which were blocking the cement pores. There was also the possibility that a high differential pressure (15MPa) meant that CO_2 came out of solution as a result of the pressure gradient, creating two-phase flow within the core, with the trapped residual CO_2 reducing the permeability.

Migration along the cement-casing interface

The cement-casing interface is another potential migration route. However, where the cement and its bond with the casing are of good quality, the effective permeability is very low along this interface. However, the presence of an annular gap produces a significant increase in effective permeability (Bachu and Bennion, 2008). Experiments by Carey et al. (2010) investigated this microannulus by embedding rectangular casing sections in cement plugs, with grooves to accommodate fluid flow. Results showed that reactions within the cement were limited to a slow diffusion of CO_2 into the matrix, and no significant cement erosion was observed over 394 hours. Degradation products from steel casing and cement dissolution were observed within the channels, again indicating the possibility of flow being limited by self-sealing carbonate deposition.

4 Conclusions

There are three main pathways for CO₂ migration from storage formations via wells; the interface between the cement and the formation, within the cement itself or the interface between the cement and well casing. While poor cementing practices during well completion may represent an important opportunity for the creation of these migration pathways, there is also potential that cement carbonation over long time periods could also create pathways in otherwise soundly cemented wells. Cement carbonation refers to the series of chemical reactions that take place when acidic waters interact with cement. During CO₂ storage dissolution of CO₂ into formation pore water leads to the formation of carbonic acid and, at least the conditions that could lead to the chemical alteration of the cement and potential dissolution of cement components. However for this reaction to take place acidic pore water must come into contact with cement. An important aspect to assessing the risk of cement degradation occurring is a consideration of the reservoir migration of CO₂ as there are complex issues related to the migration of CO₂ rich formation waters that will play a key role.

Intact adequately cured cement has a very low permeability meaning that bulk flow of water through the cement matrix is extremely limited. Additionally one of the reaction products is a solid, calcium carbonate, which precipitates and would act to lower permeability further. Thus under certain circumstances cement carbonation will be self sealing and act to prevent further cement degradation. However, this calcium carbonate can solubilise in the presence of dissolved CO₂ and thus could be removed if the pore fluids are flowing.

Previous experimental work can be divided into static experiments where cement is exposed to acidic waters in a batch reactor or dynamic experiments where water is flowed through a sample. While there have been a number of static experiments, the dynamic experiments at pressures, temperatures and water chemistries representative of reservoir conditions are much more limited. Previous dynamic work has considered the cement-casing interface and migration through fractured cement. For both cases precipitates formed during the reaction have acted to clog the migration pathways. A missing aspect to this previous work is the cement-formation interface where there is potential for flowing pore waters rich in CO₂ to come into contact with the cement. At this interface degradation products could be dissolved and removed potentially leading to an erosion of the cement over time. While experiments conducted by Duguid et al. (2011) considered the cement-formation interface these were essentially of a static nature in a batch reactor at atmospheric pressure and ambient temperature. In order to replicate the acidity of pore waters at reservoir pressures and temperatures HCl was added to the water in the experiments to lower its pH.

To conclude the previously published experimental work has informed the current project with respect to experimental methods and overall objectives. The laboratory work will build on these studies with the aim of clarifying the role of cement degradation with a particular focus on the conditions to be encountered in the National Storage Flagship storage sites. The following has been identified;

- Pressure and temperature – these are a significant influence on the CO₂ solubility and thus the concentration of carbonic acid, a key determinant in cement carbonation. It is therefore important that the test conditions are representative of the range encountered in the storage target.
- Formation water chemistry – The ionic composition of the formation water will influence the chemical reactions taking place; for example Duguid & Scherer (2010) found significant difference between artificial formation waters equilibrated with sandstone and limestone, related to the concentration of calcium carbonate.

- Monitoring methods – the previous experimental studies involved a range of monitoring techniques, including permeability with time, chemical analysis of outflow water, analysis of the core sample using x-ray diffraction to determine mineralogy.

References

- Adelaide Brighton Cement Ltd, 2007, Auswell Class G Cement, Adelaide.
- American Petroleum Institute (API), 1995, Specification for Cements and Materials for Well Cementing API Specification 10 A, 20th Ed, American Petroleum Institute (API), Northwest
- American Petroleum Institute (API), 1997, Recommended Practice for Testing Well Cements API Recommended Practice 10B, 22nd Ed, American Petroleum Institute (API), Northwest
- Bachu, S., Bennion, D. B., 2009, Experimental assessment of brine and/or CO₂ leakage through well cements at reservoir conditions, *Int. J. Greenhouse Gas Control*, 3, 494–501.
- Barlet-Gouedard, V., Rimmelé, G., Porcherie, O., Quisel, N., Desroches, J., 2009, A solution against well cement degradation under CO₂ geological storage environment, *Int. J. Greenhouse Gas Control* 3, 206-216.
- Bertos FM., Simons S.J.R., Hills C.D., Carey P.J., 2004, A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂, *J. Hazardous Materials B112* 193–205
- Carey, J. W., Wigand, M., Chipera, S. J., WoldeGabriel, G., Pawar, R., Lichtner, P. C., Wehner, S. C., Raines, M. A., Guthrie, G. D., 2007, Analysis and performance of oil well cement with 30 years of CO₂ exposure from the SACROC unit, West Texas, USA. *Int. J. Greenhouse Gas Control* 1 (1), 75–85.
- Carey, J.W., Svec, R., Grigg, R., Zhang, J., Crow, W., 2010, Experimental investigation of wellbore integrity and CO₂-brine flow along the casing-cement microannulus, *Int. J. Greenhouse Gas Control* 4, 272-282.
- Celia, M.A., Bachu, S., Nordbotten, J.M., Gasda, S.E., Dahle, H.K., 2004, Quantitative estimation of CO₂ leakage from geological storage: analytical models, numerical models and data needs, *Proc. 7th Int. Conf. Greenhouse Gas Control Technology*, Vancouver, Canada.
- Choi, Y.-S. and Netic, S. 2009. Corrosion behaviour of carbon steel in supercritical CO₂-water environments, *NACE International Corrosion 2009 Conference and Expo*, Paper 09256, Atlanta, Georgia, USA.
- Crow, W., Williams, B., Carey, J.W., Celia, M., Gasda, S., 2009, Wellbore integrity analysis of a natural CO₂ producer. *Proc. 9th Int. Conf. Greenhouse Gas Control Technologies*, Washington DC, USA.
- Duan, Z., Sun, R., Zhu, C., Chou, I-M., 2006, An improved model for the calculation of CO₂ solubility in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻, *Marine Chemistry*, 98, 131-139.
- Duguid, A., 2009. An estimate of the time to degrade the cement sheath in a well exposed to carbonated brine. *Energy Procedia* 1, 3181-3188.
- Duguid, A., Radonjic, M., Scherer, G.W., 2011, Degradation of cement at the reservoir/cement interface from exposure to carbonated brine, *Int. J. Greenhouse Gas Control* 5, 1413-1428.
- Duguid, A., Scherer, G.W., 2010, Degradation of oilwell cement due to exposure to carbonated brine. *Int. J. Greenhouse Gas Control*, 4, 546–560.
- Huerta, N.J., Bryant, S.L., Strazisar, B.R., Kutchko, B.G., Conrad, L.C., 2009, The influence of confining stress and chemical alteration on conductive pathways within wellbore cement, *Energy Procedia* 1, 3571-3578.
- Kutchko, B.G., Strazisar, B.R., Dzombak, D.A., Lowry, G.V., Thaulow, N., 2007, Degradation of Well Cement by CO₂ under Geologic Sequestration Conditions, *Environ. Sci. Technol.*, 41, 4787–4792.

- Kutchko, B.G., Strazisar, B.R., Lowry, G.V., Dzombak, D.A., Thaulow, N., 2008, Rate of CO₂ Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions, *Environ. Sci. Technol.*, 42, 6237-6242.
- Onan, D.D., 1984, Effects of Supercritical Carbon Dioxide on Well Cements, Permian Basin Oil and Gas Recovery Conference, Texas, March 8-9.
- Rimmelé, G., Barlet-Gouédard, V., Porcherie, O., Goffé, B., Brunet, F., 2008, Heterogeneous porosity distribution in Portland cement exposed to CO₂-rich fluids, *Cement and Concrete Research* 38, 1038–1048.
- Rochelle, R.A., Moore, Y.A. , 2002, The solubility of supercritical CO₂ into pure and synthetic Utsira porewater, British Geological Survey Commissioned Report CR/02/052.
- Schaef, H.T., McGrail, B.P. , 2004, Direct measurement of pH and dissolved CO₂ in H₂O-CO₂ brine mixtures to supercritical conditions, *Proc. 7th Int. Conf. Greenhouse Gas Control Technologies*, Vancouver, Canada.
- Scherer, G.W., Celia, M.A., Prévost, J.-H., Bachu, S., Bruant, R., Duguid, A., Fuller, R., Gasda, S.E., Radonjic, M., Vichit-Vadkan, W., 2005. Leakage of CO₂ through abandoned wells: role of corrosion of cement. In: *Carbon Dioxide Capture for Storage in Deep Geologic Formations— Results from the CO₂ Capture Project, Vol 2—Geologic Storage of Carbon Dioxide with Monitoring and Verification*. Elsevier Science, Amsterdam.
- Short, N.R., Purnell, P., Page, C.L., 2001. Preliminary investigations into the supercritical carbonation of cement pastes. *J. Materials Science* 36, 35-41.
- Strazisar, B., Kutchko, B. , Huerta, N. , 2009, Chemical Reactions of Wellbore Cement Under CO₂ Storage Conditions: Effects of Cement Additives, *Energy Procedia* 1:3603-3607.
- Taylor H. F.W., 1997, *Cement Chemistry*, Thomas Telford Publishing, 2nd Ed, London
- Wigand, M., Kaszuba, J.P., Carey, J.W., Hollis, W.K., 2009, Geochemical effects of CO₂ sequestration on fractured wellbore cement at the cement / caprock interface, *Chemical Geology* 265, 122-133.
- Yalcinkaya, T., Radonjic, M., Hughes, R.G., Willson, C.S., Ham, K., 2011, The effect of CO₂-saturated brine on the conductivity of wellbore-cement fractures , *SPE Int. Conf. on CO₂ Capture, Storage and Utilization*, New Orleans, Louisiana, USA, 10-12 November, 2010. SPE 139713.